

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



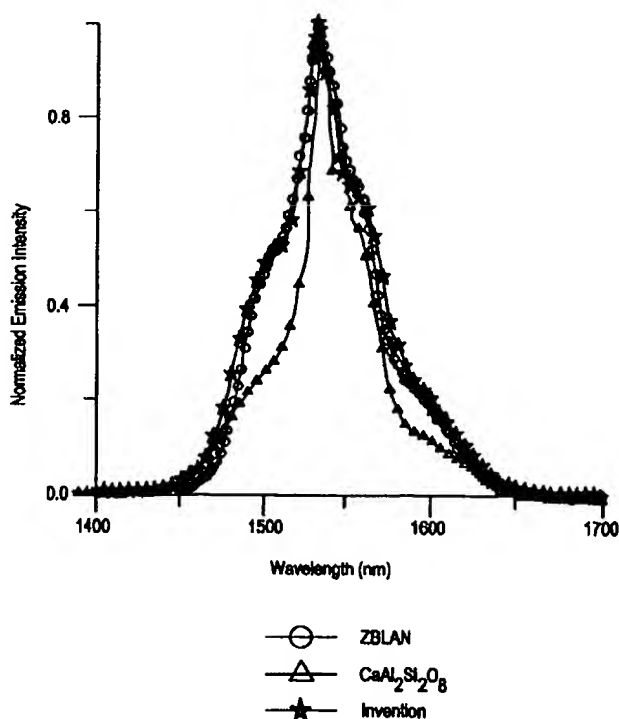
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 13/04		A1	(11) International Publication Number: WO 99/51537
			(43) International Publication Date: 14 October 1999 (14.10.99)
(21) International Application Number: PCT/US99/07765		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 8 April 1999 (08.04.99)			
(30) Priority Data: 60/081,073 8 April 1998 (08.04.98) US			
(71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).		Published With international search report.	
(72) Inventors; and (75) Inventors/Applicants (for US only): DICKINSON, James, E. [US/US]; 202 Wall Street, Corning, NY 14830 (US). ELLISON, Adam, J. [US/US]; 146 East Third Street, Corning, NY 14830 (US). MAYOLET, Alexandre, M. [FR/FR]; 91, rue de Rechevres, R-28000 Chartres (FR). PRASSAS, Michel [FR/FR]; 16, rue Saint-Eloi, R-77870 Vulaines sur Seine (FR).			
(74) Agent: GREENER, William; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).			

(54) Title: ANTIMONY OXIDE GLASS WITH OPTICAL ACTIVITY

(57) Abstract

A glass consisting essentially of antimony oxide. An optically active glass consisting essentially of antimony oxide and up to about 4 mole % of an oxide of a rare earth element. A rare earth-doped, antimony oxide-containing glass including 0-99 mole % SiO₂, 0-99 mole % GeO₂, 0-75 mole % (Al, Ga)₂O₃, 0.5-99 mole % Sb₂O₃, and up to about 4 mole % of an oxide of a rare earth element. The oxide of the rare earth element may comprise Er₂O₃. The glass of the invention further includes fluorine, expressed as a metal fluoride. An optical energy-producing or light-amplifying device, in particular, an optical amplifier, comprising the above-described glass. The optical amplifier can be either a fiber amplifier or a planar amplifier, either of which may have a hybrid composition. Embodiments of the glass of the invention can be formed by conventional glass making techniques, while some of the high content antimony oxide embodiments are formed by splat or roller quenching.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GR	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

ANTIMONY OXIDE GLASS WITH OPTICAL ACTIVITY

This application claims priority to US Provisional application (Dickinson 15) filed on April 8, 1999 which is herein incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to antimony oxide-containing glass compositions and, more particularly, to optically active antimony oxide-containing glasses that are optically active by being doped with a rare earth element; their use in optical amplifying devices and optical amplifying devices incorporating these compositions; and methods for making the glass compositions of the invention. As used herein, the term "optically active" refers to a rare earth doped glass capable of stimulated emission for amplifying a light signal when the glass is excited by a suitable pumping source.

2. Technical Background

Recently, transparent materials capable of efficient frequency upconversion, in particular, various rare earth ion-doped fluoride glasses and crystals, have received much attention because of their potential use in blue or green solid state lasers. Single mode optical fibers doped with low levels of rare-earth ions can be drawn from fluoride glasses, bringing about highly efficient blue or green upconversion fiber lasers. Unfortunately, heavy metal fluoride glasses suffer certain undesirable attributes that have restricted their applications. Most notably, heavy metal fluoride glasses exhibit poor resistance to devitrification. Mimura *et al.* discusses the crystallization problems

of heavy metal fluoride glasses, one example of which is referred to as ZBLAN, and the light scattering problems resulting therefrom.

The susceptibility of heavy metal fluoride glasses to devitrification generates problems in making large preforms. Crystallization in the preform causes difficulties during the formation of optical fibers by commonly used methods. Heavy metal fluoride glasses are quite prone to inhomogeneous nucleation, which leads to crystallization at the core and cladding interfaces during the drawing of the optical fiber. The resulting crystals in the fibers cause serious light scattering losses.

Devitrification of the heavy metal fluoride glasses is aggravated when ions necessary to impart differences in indices of refraction to the core and cladding are added to the glass composition. Additional doping, for example, with rare earth metal ions, also tends to reduce the stability of the glass. As a consequence of those problems, research has focused on finding additives to a base fluoride glass composition that will reduce the tendency of the glass to devitrify and to increase the chemical stability thereof. In addition, the preparation of fluoride glasses requires that the glass forming components be reheated at high temperatures. Furthermore, these glasses cannot be melted in air but require a water-free, inert gas environment.

Most oxide glasses such as, for example, silicon dioxide, are easier to prepare, more chemically and mechanically stable, and more easily fabricated into rods, optical fibers, or planar waveguides than are fluoride glasses. Unfortunately, because of their higher phonon energy, silica glasses are very inefficient for infrared upconversion. Addition of even small amounts of oxides into fluoride glasses to improve their stability significantly quenches their upconversion luminescence.

One author describes a class of infrared ("IR") upconversion materials prepared from classical glass-forming oxides (SiO_2 , GeO_2 , P_2O_5 , etc., containing PbF_2 and rare earth oxides). These materials show an efficiency nearly twice as high as a $\text{LaF}_3\text{:Yb:Er}$ phosphor, but, because they are inhomogeneous and include both a glassy phase and a crystalline phase containing large (ca 10 μm) embedded crystals, they are not transparent.

Another reference describes transparent oxyfluoride vitroceramics (also called glass ceramics) containing oxides of high phonon energy like SiO_2 and $\text{AlO}_{1.5}$ but showing IR to visible upconversion that are more efficient than fluoride glass. A reported typical composition consists essentially, expressed in terms of mole percent,

of: SiO_2 , 30; $\text{AlO}_{1.5}$, 15; PbF_2 , 24; CdF_2 , 20; YbF_3 , 10; ErF_3 , 1. Heat treatment of that composition at 470°C causes the formation of microcrystallites, which are reported not to reduce the transparency of the body. It is further asserted that the Yb^{3+} and Er^{3+} ions are preferentially segregated from the precursor glass and dissolved into the microcrystals upon heat treatment. The microcrystallites are reported to be about 20 nm in size, small enough that light loss from scattering is minimal. The upconversion efficiency of their products is said to be about 2 to 10 times as high as that measured on the precursor glass and other fluoride-containing glasses. However, the crystals that are formed in the reported glass have a cubic lattice structure, which limits the concentration of some of the trivalent rare-earth elements that can be incorporated into the glass ceramic. Another problem with these materials is that their formulation requires cadmium, a carcinogen whose use is restricted. Furthermore, the reported glass-ceramic does not appear to have a broad, flat emission spectrum required for some optical amplifier applications.

Rare earth-doped glasses have found frequent use for the fabrication of light-generating and light-amplifying devices. For example, Snitzer describes a laserable glass comprising a host material that contains a fluorescent trivalent neodymium ingredient. Desurvire *et al.* describe an optical amplifier comprising a single mode fiber that has an erbium-doped core. da Silva *et al.* describe an apparatus and method for flattening the gain of an optical amplifier that utilizes an erbium-doped silica fiber having a germanosilicate core. Bruce *et al.* describe an erbium-doped planar optical device whose active core includes a mixture of oxides such as lanthanum and aluminum oxides. The inclusion of antimony oxide in glasses for optical devices is also reported. One reference describes a glass for use in waveguides that contains 50-75 mol % $\text{SbO}_{1.5}$.

For the construction of efficient optical amplifiers, there remains a need for new, readily prepared glasses that display an optimal combination of gain flatness and breadth. This need is well met by the glass of the present invention.

SUMMARY OF THE INVENTION

The present invention is directed to an optically active glass containing Sb_2O_3 and up to about 4 mole % of an oxide of a rare earth element. All constituents listed herein are expressed in mole percentages on an oxide basis. An undoped, nonactive base glass may consist essentially of Sb_2O_3 . Its active form may consist essentially of Sb_2O_3 and up to about 4% RE_2O_3 , where RE is a rare earth element. A glass comprising Sb_2O_3 and up to about 4% RE_2O_3 can preferably include 0-99% percent SiO_2 , 0-99% GeO_2 , and 0-75% (Al_2O_3 or Ga_2O_3). In addition, any of the glass compositions described herein may contain up to 10 mole % B_2O_3 substituted for an equivalent amount of Sb_2O_3 .

Although the glass of the present invention is highly desirable because it can be fabricated in air using standard melting techniques and batch reagents, when the glass contains about 90% or more of Sb_2O_3 it is formed by the techniques of splat quenching or roller quenching. The glass composition of the present invention exhibits a gain spectrum with excellent breadth and flatness characteristics and can be readily modified for specific optical amplifier applications.

Further in accordance with the present invention is an optical energy producing or light-amplifying device, in particular an optical amplifier, that comprises the glass of the invention. The optical amplifier can be either a fiber amplifier or a planar amplifier, either of which may be of a hybrid (composition) construction.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a graph comparing the emission spectra from 1400 nm to 1700 nm of an aluminosilicate glass, a fluoride glass (ZBLAN), and an erbium-doped, antimony-containing glass of the invention;

FIG. 1B is a detailed version of FIG. 1A over the range 1500 nm to 1600 nm;
FIG. 2 is a plot of the calculated gain spectra for a glass of the invention; and
FIG. 3 is a graph of the calculated gain spectra for 61-65% inversion in 0.5% steps for a glass of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The optically active glass of the present invention expressed in mole percent on an oxide basis comprises Sb_2O_3 and up to about 4 mole % of an oxide of a rare earth

element. The glass preferably comprises 0.5-99 mole % Sb_2O_3 , and preferably about 0.1-0.2 mole % Er_2O_3 . The glass further preferably comprises a remainder of one or more compatible metal oxides.

5 In a preferred embodiment, the optically active glass consists essentially of Sb_2O_3 and up to about 4% Re_2O_3 , where Re is an oxide of a rare earth element. Although erbium is the especially preferred rare earth, the glass may comprise other rare earth elements to impart optical activity to the glass as defined herein, as further described below.

10 It will be appreciated by those skilled in the art that the rare earth plays no part in forming the glass *per se*. Thus an embodiment of the invention is a glass consisting essentially of Sb_2O_3 .

The glass of the invention can further comprise 0-99% SiO_2 , 0-99% GeO_2 , and 0-75% (Al_2O_3 or Ga_2O_3).

15 In an aspect of each of the embodiments of the invention, up to 10 mole % B_2O_3 can be substituted for an equivalent amount of Sb_2O_3 . The effect of B_2O_3 is at least two-fold: disadvantageously it reduces the lifetime of the emission at 1530nm, however, more importantly, however, it apparently reduces the τ_{32} lifetime (980nm pumping metastable level) at a faster rate which is preferable for pumping an erbium-doped optical amplifier made from the glass compositions of the invention at 980nm.

20 The glass of the invention can further comprise 0-45 mol % A_2O , where A is Li, Na, K, Rb, Cs, or mixtures thereof, and/or 0-45 mol % MO , where M is Mg, Ca, Sr, Zn, Ba, Pb, or mixtures thereof. The rare earth element is Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or mixtures thereof, and Scandium (Sc) may be substituted for a rare earth in an embodiment of the invention. In one preferred
25 embodiment of the present invention, the glass comprises 50-72 mol % SiO_2 , 10-20 mol % Al_2O_3 , 10-30 mol % Sb_2O_3 , 10-20 mol % K_2O , and about 0.1 mol % Er_2O_3 .

In another preferred embodiment of the present invention, the glass further comprises a metal fluoride, bromide, chloride, or mixtures thereof. The metal can be a trivalent, divalent, or monovalent metal, or mixtures thereof. In a further preferred
30 embodiment, the metal halide is a metal fluoride such as Al_2F_6 , CaF_2 , K_2F_2 , or mixtures

thereof. The (metal fluoride)/(metal fluoride + total oxides) molar fraction of the glass is preferably about 0.01 to 0.25, more preferably about 0.1 to 0.2.

In a further preferred embodiment of the present invention, the glass comprises 50-72 mol % SiO_2 , 10-20 mol % Al_2O_3 , 10-30 mol % Sb_2O_3 , 10-20 mol % K_2O , and about 0.1 mol % Er_2O_3 , and further includes 5-20 mol % of a metal halide.

Further in accordance with the present invention is an optical energy-producing or -amplifying device. Preferably, the device is an optical amplifier comprising the rare earth element-doped, antimony oxide containing glass described above. The optical amplifier can be either a fiber amplifier or a planar amplifier, as described in, for example, U.S. Patent Nos. 5,027,079, 5,239,607, and 5,563,979, the disclosures of which are incorporated herein by reference. The fiber amplifier can further be of a hybrid structure that combines legs formed from a glass of the invention with legs formed from a standard aluminosilicate glass, as described, for example, in M. Yamada et al., "Flattening the gain spectrum of an erbium-doped fiber amplifier by connecting an Er^{3+} -doped SiO_2 - Al_2O_3 fiber and an Er^{3+} -doped multicomponent fiber," Electronics Lett., **30**, pp 1762-1764 (1994), the disclosure of which is incorporated herein by reference.

As discussed in the commonly-assigned, previously-filed, co-pending provisional application by Dickinson et al., RARE EARTH ELEMENT-HALIDE ENVIRONMENTS IN OXYHALIDE GLASSES, Serial No. 60/067245, filed December 2, 1997, the disclosure of which is incorporated herein by reference, the local bonding environments of rare earth elements ("REE") in glasses determine the characteristics of their emission and absorption spectra. Several factors influence the width, shape, and absolute energy of emission and absorption bands, including the identity of the anion(s) and next-nearest-neighbor cations, the symmetry of any particular site, the total range of site compositions and symmetries throughout the bulk sample, and the extent to which emission at a particular wavelength is coupled to phonon modes within the sample. Fluoride glasses are useful hosts for optically active REE, because the fluorine atoms surrounding the REEs substantially impact REE emission and absorption spectra. The extreme electronegativity of fluorine lifts the degeneracy of the electronic states of the REE, producing emission and absorption

bands that differ substantially from those produced in oxide hosts, being broader and having different relative intensities and, sometimes, different positions. They are also often blue-shifted relative to their positions in oxide glasses. In general, the absolute position and width of an emission or absorption band shifts to lower energy as the electronegativity of the surrounding anions decreases: for example, the total bandwidth of the Er^{3+} 1530 nm emission band in fluoride glasses, such as ZBLAN, is greater than in nearly any oxide glass, and the high-energy edge of the emission band in a fluoride glass is at a higher energy than in an oxide glass. In certain systems, such as hybrid oxyfluoride glasses, it is possible to obtain much of the bandwidth and gain flatness of a fluoride glass by creating environments for the REE that are a combination of oxide and fluoride-like sites.

For optical amplifier applications, the region over which a convolution of the emission and absorption is the flattest is the optimal window through which to pass signals. Because both the position of the overall emission bands and the structure within the band vary from fluoride to oxide hosts, the window with optimal gain flatness also varies. Ideally, one would like to obtain the broadest emission possible in a single glass.

Relative to oxide glasses, fluoride glasses also can accommodate very high concentrations of REE without incurring nonradiative losses resulting from energy transfers between the REE. However, fluoride glasses must be prepared under controlled atmospheres; they have extremely high coefficients of thermal expansion and are environmentally unstable compared to many oxide glasses, which complicates their use in practical applications. Ideally, glasses that produce the fluoride-like environments for REE while retaining the physical and chemical characteristics of oxide glasses are desired.

As noted above, glasses having a broad, flat emission spectra are highly desirable for optical amplifier applications. A flat emission spectrum is defined as one having less than 10% gain ripple over bands (or windows) up to 38 nm wide. Inclusion of fluorine in a glass results in improved dispersal of the REE throughout the glass, which facilitates higher REE loadings without degradation of lifetime. Higher concentrations of REE that are dispersed in separate locations and are thus unable to

physically interact with each other are believed possible. The REE include Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. In an aspect of the invention, Sc may be substituted for a rare earth element. In accordance with the present invention, Er is especially preferred.

5 The rare earth element ions in the glass matrix of the present invention are dispersed in at least two distinct locations that can be characterized as either fluoride sites or oxide sites. The REE ions present in either of these two locations are unable to interact with those in the other, which allows higher loadings of REE. Accordingly, the use of the glass of the invention makes it possible to reduce the size of an optical
10 amplifier because less waveguide material for the same amount of gain is required. Furthermore, because the glass of the present invention can provide quantum efficiency upon radiation substantially equal to 100%, less powerful pump lasers are required to generate fluorescent emission. Useful fluorescent emission maxima are in the range of about 1.3 μm to about 1.8 μm . Fluorescent emission maxima of Er-doped glasses are
15 typically in the range of about 1.5 μm to about 1.6 μm .

As is well known in the art, Er-doped amplifiers are typically pumped in the 980nm or 1480nm wavelength band. In a preferred aspect of an optical amplifier embodiment of the invention for signal amplification in the 1500nm telecommunications window (C-band) and/or in the extended erbium spectrum from
20 about 1565-1610nm (L-band), pumped at 980nm, up to 10 mole % B_2O_3 is substituted for an equivalent amount of Sb_2O_3 . As stated above, the B_2O_3 reduces the τ_{32} lifetime which is advantageous for pumping an erbium-doped optical amplifier made from the glass compositions of the invention at 980nm. In a further preferred aspect of an optical amplifier embodiment of the invention, up to 15 mole % As_2O_3 (arsenic-
25 trioxide), up to 15 mole % Tl_2O (thallium oxide), up to 15 mole % In_2O_3 (indium oxide), and up to 15 mole % Bi_2O_3 (bismuth trioxide), can be included in the compositions of the invention to modify physical properties such as refractive index and viscosity with no adverse effect on amplifier performance.

Substitutions of germanium and lead for silicon or gallium for aluminum can be
30 used to improve fluorescence intensities and emission lifetimes, and also to modify liquefaction temperatures, viscosity curves, expansivity, and refractive index. Alkali

and alkaline earth metals can be included in the glass to vary the refractive index and to increase or decrease thermal expansivity. Glasses containing optically active REE can be co-doped with non-active REE (for example, Er co-doped with La or Y) to increase emission lifetimes, or co-doped with optically active REE (such as Er co-doped with Yb) to improve quantum efficiency. By varying bulk composition, glasses can be formed with optical properties transitional between pure fluoride and pure oxide glasses, thus affording maximum flexibility in optical properties.

The glass of the present invention has absorption and emission characteristics that are effectively hybrids of the best characteristics obtained in oxide or fluoride glasses alone. However, unlike fluoride glasses, which must be prepared in an inert atmosphere, embodiments of the glass of the present invention can be fabricated in air using standard melting techniques and batch reagents. In addition, the environmental stability of the hybrid glasses considerably exceeds that of pure fluoride glasses. Moreover, the addition of fluorine allows the glass matrix to obtain much of the bandwidth and gain flatness of a fluoride glass by creating environments for the REE that are a combination of oxide- and fluoride-like sites.

The properties of the glass of the present invention make it particularly useful for the fabrication of a variety of optical devices. Provided with a compatible covering or cladding, the glass can be formed into fiber or planar optical amplifiers or lasers. It can be used alone in planar amplifier applications, or in combination with chlorine-free oxyfluoride clad glasses for double-crucible fiberization or rod-and-tube redraw. In addition, the emission/absorption spectra of glasses prepared in accordance with the invention may be tailored to "fill in holes" in the gain spectrum of conventional amplifier materials such as silica or ZBLAN, for example, resulting in hybrid amplifiers that provide a greater degree of gain flatness than can be obtained from any of these materials alone.

Embodiments of the glass of the invention can generally be produced according to standard techniques for making glasses: providing glass-forming components and treating these components under conditions effective to produce the glass, which generally entails melting the glass-forming components to produce a glass melt, forming the glass melt into a shaped article, which is then cooled. Preferably, the

components are melted at a temperature of about 1300-1500°C for about 2 hours to 4 hours to produce the glass melt. Next, the glass melt is formed into a shaped article by forming procedures such as, for example, rolling, pressing, casting, or fiber drawing. A shaped article such as, for example, a patty, rod, or sheet, is cooled and then annealed at a temperature of about 350-450°C for about 0.5 hour to 2 hours. After the final heat treatment, the shaped article is allowed to cool to room temperature.

Certain embodiments of the glass compositions of the present invention, namely those including about 90 mole % or more Sb_2O_3 , were prepared by splat quenching or roller quenching. Since antimony is not compatible with platinum, the high content antimony oxide glasses of the invention are melted in silica or alumina crucibles. During heat up, some of the Sb_2O_3 changes to Sb_2O_5 , and on cooling forms the very refractory crystalline phase cervantite, Sb_2O_4 . This problem is alleviated by splat and/or roller quenching as described in Examples 1-3, below. A possible alternative is to melt Sb_2O_3 in a dry box, known to those skilled in the glass forming art.

Table I lists some preferred exemplary compositional embodiments of the invention.

TABLE I

Sb_2O_3	SiO_2	GeO_2	Al_2O_3	Ga_2O_3	Cs_2O	In_2O_3	Na_2O	K_2O	F	RE_2O_3
90	9.9									0.1
90		9.9								0.1
5	94.9									0.1
5		94.9								0.1
35			25			38				2
35				25		38				2
75						24.9				0.1
30						69.9				0.1
99.9										0.1
30.3		60.6	3.03	1.52		1.52	1.52	1.52	1	1
27.77		55.54	4.63	4.63		4.63	1.4	1.4	1	1

EXAMPLES

The following examples further illustrate the invention:

Example 1-3: Preparation of Erbium-Doped, Antimony Oxide-Containing Glass

Example 1: The following composition

Sb_2O_3 99.0 mol%

Er_2O_3 0.1 mol%

was prepared as follows: A 25g charge of melt was held at 25-50°C above its liquidus until it reached thermal equilibrium, about 10-15 min.

In a preferred method aspect for forming this glass by splat quenching, the charge is delivered to a cold plate (e.g., steel or graphite) and smashed from above by a cold "hammer" (e.g., steel or graphite). With a good configuration, the quench rate is $\geq 250^\circ\text{C}/\text{sec}$.

In another preferred method aspect for forming this glass by roller quenching, the charge is delivered between cold rollers (e.g., steel or graphite). Depending upon the thermal conductivity of the sample, the quench rate is $\gg 1000^\circ\text{C}/\text{s}$, comparable to quench rates obtained in fiberization.

Larger melt samples of the glass can be similarly processed, but the lateral dispersal of the melt in the splat quench limits the largest size that can be handled to about 150g. The glass in a roller quench operation is delivered as a continuous stream, thus there is no size limit.

Example 2: The following composition

Sb_2O_3 90.0 mol%

SiO_2 9.9 mol%

Er_2O_3 0.1 mol%

was prepared by splat quenching as described in Example 1, above.

Example 3: The following composition

Sb_2O_3 99.0 mol%

GeO_2 9.9 mol%

Er_2O_3 0.1 mol%

was prepared by splat quenching as described in Example 1, above.

Example 4: A glass-forming mixture having the following composition (in mol %) is ball-milled and charged into a silica crucible:

SiO_2	55
Al_2O_3	10.4
Al_2F_6	5

5	K ₂ O	0.6
	K ₂ F ₂	10.5
	K ₂ Br ₂ *	1.5
	Sb ₂ O ₃	17
	Er ₂ O ₃	0.1

*added to eliminate water from final glass

The crucible is covered and heated at a temperature of about 1425° C for about 2 hours.

10 The melt is poured onto a steel plate to form a sheet, which is cooled, then placed in an annealing oven and held at a temperature of about 450° C for about one hour before being allowed to cool gradually to room temperature.

Example 5: Spectroscopic Analysis of Glass Samples

15 The absorption spectra of polished 10 x 10 x 20-mm samples of the glass prepared as described in Example 4, an aluminosilicate glass (CaAl₂Si₂O₈), and a fluoride glass (ZBLAN) are measured using a Nicolet (Madison WI) FT-IR spectrophotometer with 4 cm⁻¹ resolution, 256 FID's per sample being collected. The Er fluorescence emission spectra is generated by pumping the 520 nm absorption band
20 with a Xenon lamp, and the 1.5 μm emission is measured using a liquid nitrogen-cooled Si detector together with a SPEX Fluorolog (Edison NJ) spectrophotometer. Data are collected over the range 1400-1700 nm in 0.5 nm steps, 1.5 seconds/step. Each spectrum is corrected by subtraction of the background, then normalized to a value of 1.0 for the maximum peak intensity.

25 The spectra so obtained for the three samples over the range 1400-1700 nm are depicted in FIG. 1A; a detail for the range 1500-1600 nm is shown in FIG. 1B. The breadth of the spectrum of the glass of the present invention greatly exceeds that of the aluminosilicate glass and also exceeds that of ZBLAN in the peak region around 1530-1560 nm by about 7 nm.

30

Example 6: Determination of Gain Flatness for Erbium-Doped, Antimony Oxide-Containing Glass

For a sample of the glass prepared as described in Example 4, gain spectra are calculated, in steps of 10%, for levels of inversion ranging from zero to 100%. The
35 plots of the resulting spectra are shown in FIG. 2. Gain spectra are also calculated for

inversion levels over the range 61-65%, in steps of 0.5%. The percentages of inversion are calculated assuming that the absolute absorption and emission intensity maxima are of equal magnitude. The resulting plots are shown in FIG. 3.

A figure of merit (FOM) of gain flatness is defined as $(\text{MAX}-\text{MIN})/\text{MIN}$, where MAX and MIN are, respectively, the largest and smallest values for gain within a "window," or specified wavelength range. for the glass of Example 4, FOMs are calculated for "floating windows" of widths 30, 35, and 40 nm; the results are shown in Table II.

Table II

<u>Window width (nm)</u>	<u>Wavelength range (nm)</u>	<u>% Inversion</u>	<u>FOM</u>
30	1535-1565	63	7
35	1530-1565	63	7
40	1528-1568	63.5	14.5

As shown by the data of Table II, the calculated gain spectra show a very flat response ($\text{FOM} = 7$, corresponding to a 7% gain ripple) for the 30 and 35 nm windows, which is substantially maintained for a window of 38 nm width. Even for the 40 nm-wide window, a desirably flat response ($\text{FOM} = 14.5$, ca 15% gain ripple) is maintained. These excellent gain flatness results greatly exceed those attainable with previously known silica amplifier materials.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention that is defined by the following claims.

WHAT IS CLAIMED:

1. An optically active glass (in mole % on an oxide basis), comprising:
Sb₂O₃; and
5 up to about 4% of at least one of RE₂O₃, where RE is a rare earth element, and Scandium.
2. The glass of claim 1, further comprising a remainder of a compatible metal oxide.
- 10 3. The glass of claim 1 wherein Sb₂O₃ is 0.5-99%.
4. The glass of claim 1 further comprising:
0-99% SiO₂;
15 0-99% GeO₂; and
0-75% (Al₂O₃ or Ga₂O₃).
5. The glass according to claim 4 further comprising:
10-80 mol % SiO₂, 5-30 mol % Al₂O₃, 5-50 mol % Sb₂O₃, and about 0.1-
20 0.2 mol % Er₂O₃.
6. The glass according to claim 5 further comprising:
50-72 mol % SiO₂, 10-20 mol % Al₂O₃, 10-30 mol % Sb₂O₃, 10-20 mol
25 % K₂O, and about 0.1 mol % Er₂O₃.
7. The glass according to claim 6 further comprising:
5-20 mol % of a metal halide selected from the group consisting of a
metal fluoride, a metal bromide, a metal chloride, and mixtures thereof, wherein said
metal is a trivalent metal, a divalent metal, a monovalent metal, and mixtures thereof.
- 30 8. The glass according to claim 7 wherein said metal halide is a metal
fluoride selected from the group consisting of AlF₃, CaF₂, K₂F₂, and mixtures thereof.

9. The glass of claim 4 further comprising:

0-75% A_2O , where A is selected from the group consisting of Li, Na, K, Rb, Cs, and mixtures thereof.

5

10. The glass of claim 4, further comprising:

0-15% As_2O_3 ;

0-15% Tl_2O ;

0-15% In_2O_3 , and

10

0-15% Bi_2O_3 .

11. The glass of claim 4 wherein 0-10 mole % B_2O_3 is substituted for an equivalent amount of Sb_2O_3 .

15

12. The glass according to claim 4 further comprising:

0-45 mol % MO , where M is selected from the group consisting of Mg, Ca, Sr, Zn, Ba, Pb, and mixtures thereof.

20

13. The glass according to claim 4 wherein the rare earth element is selected from the group consisting of Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and mixtures thereof.

14. The glass according to claim 13 wherein the oxide of said rare earth element comprises Er_2O_3 .

25

15. The glass according to claim 14 further comprising about 0.05-0.4 mol % Er_2O_3 .

30

16. The glass according to claim 1 further comprising a metal halide selected from the group consisting of a metal fluoride, a metal bromide, a metal chloride, and mixtures thereof, wherein said metal is selected from the group consisting of a trivalent metal, a divalent metal, a monovalent metal, and mixtures thereof.

17. The glass according to claim 16 wherein said metal halide is a metal fluoride selected from the group consisting of Al_2F_6 , CaF_2 , K_2F_2 , and mixtures thereof.

5 18. The glass according to claim 17 having a (metal fluoride)/(metal fluoride + total oxides) molar fraction of about 0.01 to 0.25.

19. The glass according to claim 18 wherein said fraction is about 0.1 to 0.25.

10 20. A method of making the glass of claim 1, comprising at least one of the steps of:

splat quenching the glass; and

roller quenching the glass.

15 21. A glass consisting essentially of Sb_2O_3 .

22. A method of making the glass of claim 21, comprising at least one of the steps of:

20 splat quenching the glass; and

roller quenching the glass.

23. An optically active glass consisting essentially of Sb_2O_3 and up to about 4% RE_2O_3 , where RE is a rare earth element.

25 24. A method of making the glass of claim 23, comprising at least one of the steps of:

splat quenching the glass; and

roller quenching the glass.

30

25. An optical energy-producing or light-amplifying device comprising the glass according to claim 11.

26. The device according to claim 25 wherein said glass further comprises:
5 0-45 mol % A_2O , where A is selected from the group consisting of Li, Na, K, Rb, Cs, and mixtures thereof.

27. The device according to claim 25 wherein said glass further comprises:
10 0-45 mol % MO , where M is selected from the group consisting of Mg, Ca, Sr, Zn, Ba, Pb, and mixtures thereof.

28. The device according to claim 25 wherein said rare earth element is selected from the group consisting of Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and mixtures thereof.

15 29. The device according to claim 28 wherein the oxide of said rare earth element comprises Er_2O_3 .

20 30. The device according to claim 25 wherein said glass further comprises:
5-20 mol % of a metal halide selected from the group consisting of a metal fluoride, a metal bromide, a metal chloride, and mixtures thereof, wherein said metal is selected from the group consisting of a trivalent metal, a divalent metal, a monovalent metal, and mixtures thereof.

25 31. The device according to claim 30 wherein said metal halide is a metal fluoride selected from the group consisting of Al_2F_6 , CaF_2 , K_2F_2 , and mixtures thereof, and said glass has a (metal fluoride)/(metal fluoride + total oxides) molar fraction of about 0.01 to 0.25.

30 32. The device according to claim 25 wherein said glass further comprises:
10-80 mol % SiO_2 , 5-30 mol % Al_2O_3 , 5-50 mol % Sb_2O_3 , and about 0.1-0.2 mol % Er_2O_3 .

33. The device according to claim 32 wherein said glass further comprises:
50-72 mol % SiO_2 , 10-20 mol % Al_2O_3 , 10-30 mol % Sb_2O_3 , 10-20 mol
% K_2O , and about 0.1 mol % Er_2O_3 .

5 34. The device according to claim 33 wherein said glass further comprises:
5-20 mol % of a metal halide selected from the group consisting of a
metal fluoride, a metal bromide, a metal chloride, and mixtures thereof, whereof said
metal is selected from the group consisting of a trivalent metal, a divalent metal, a
monovalent metal, and mixtures thereof.

10 35. The device according to claim 34 wherein said metal halide is a metal
fluoride selected from the group consisting of Al_2F_6 , CaF_2 , K_2F_2 , and mixtures thereof.

15 36. The device according to claim 25 wherein said amplifier is one of a fiber
amplifier and a planar amplifier.

37. The device according to claim 36 wherein said amplifier is a hybrid
composition.

20 38. The device according to claim 25 exhibiting a fluorescence emission
spectrum with a maximum at about 1.5 μm to about 1.6 μm .

39. The device according to claim 25 further comprising:

25 0-15% As_2O_3 ;

0-15% Tl_2O ;

0-15% In_2O_3 , and

0-15% Bi_2O_3 .

FIG. 1A

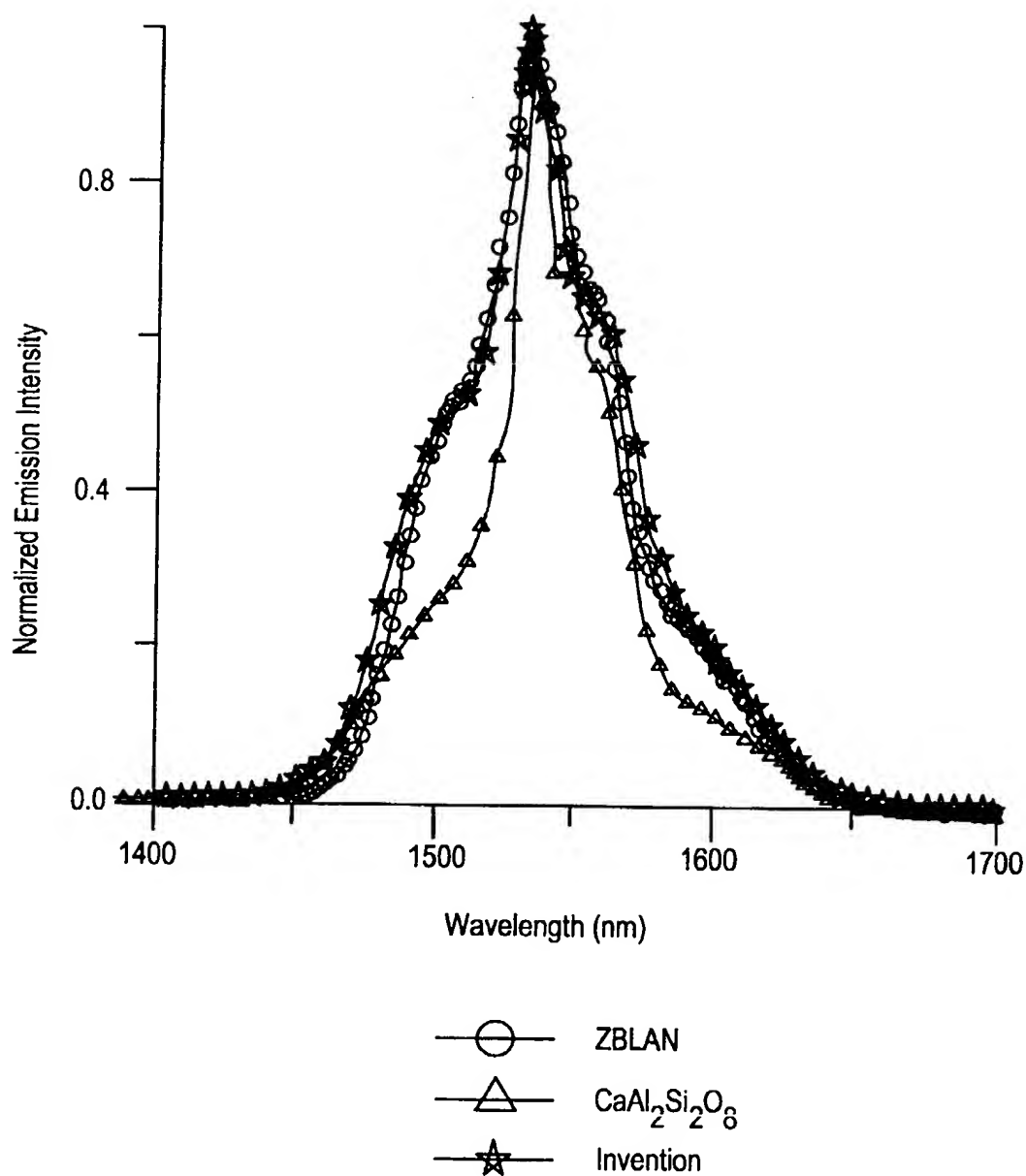


FIG. 1B

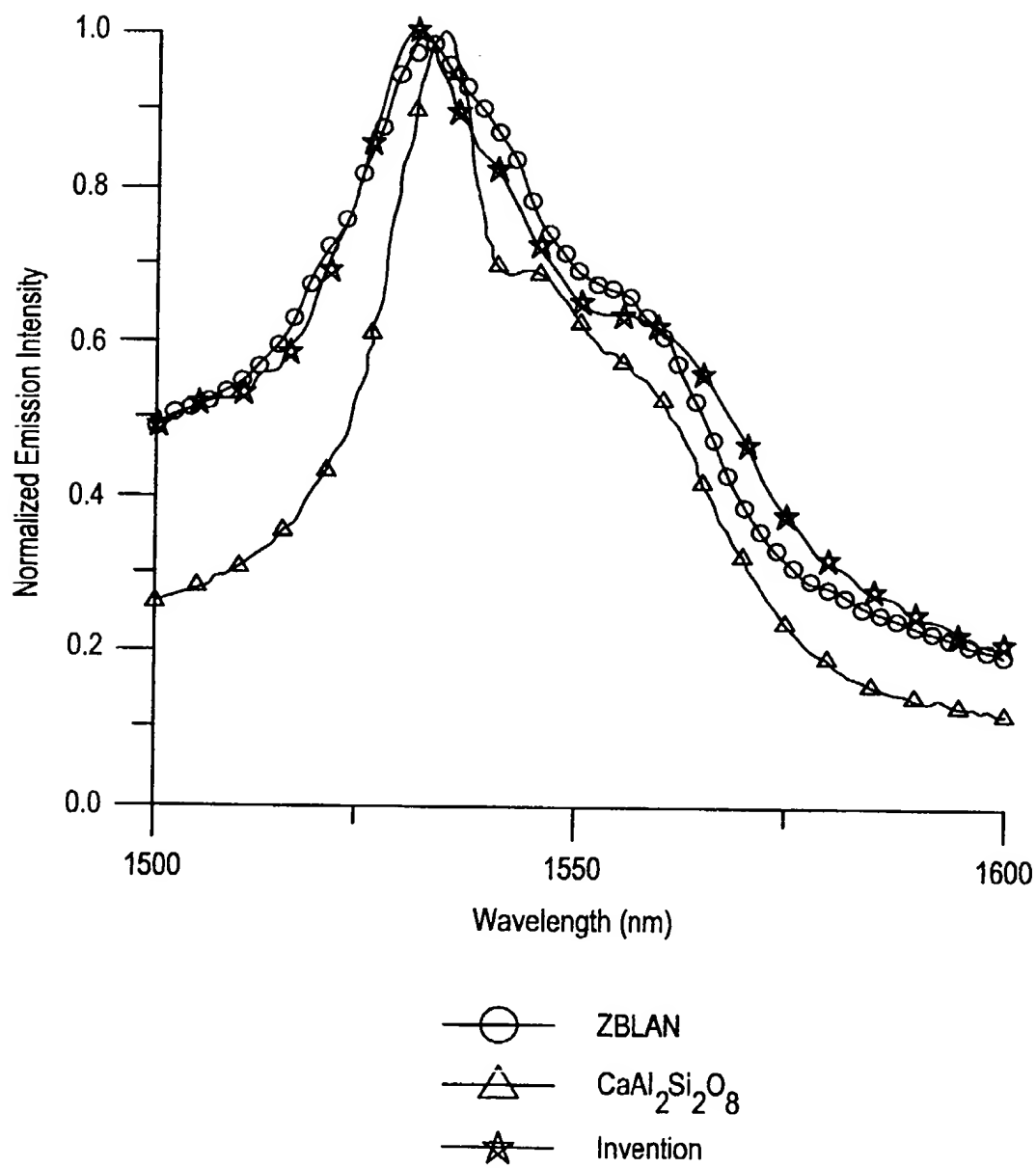


FIG. 2

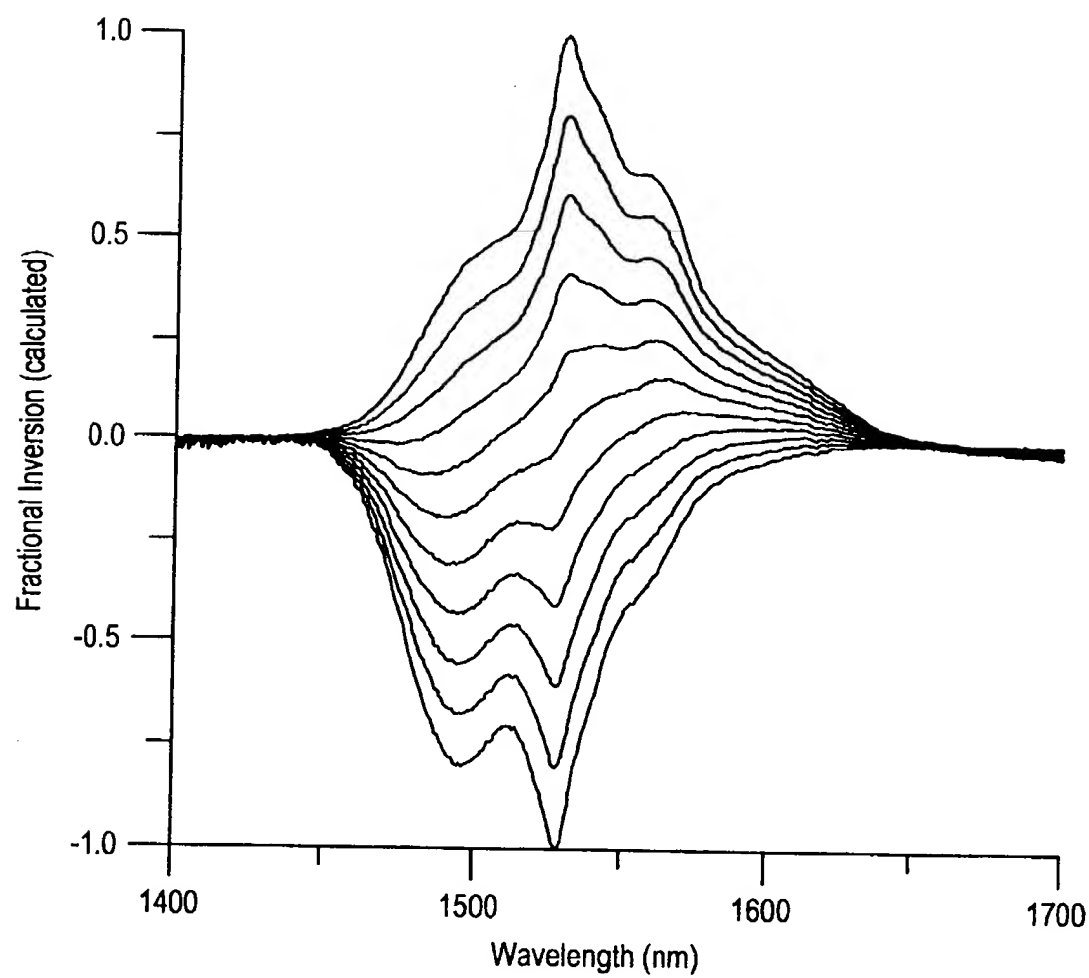
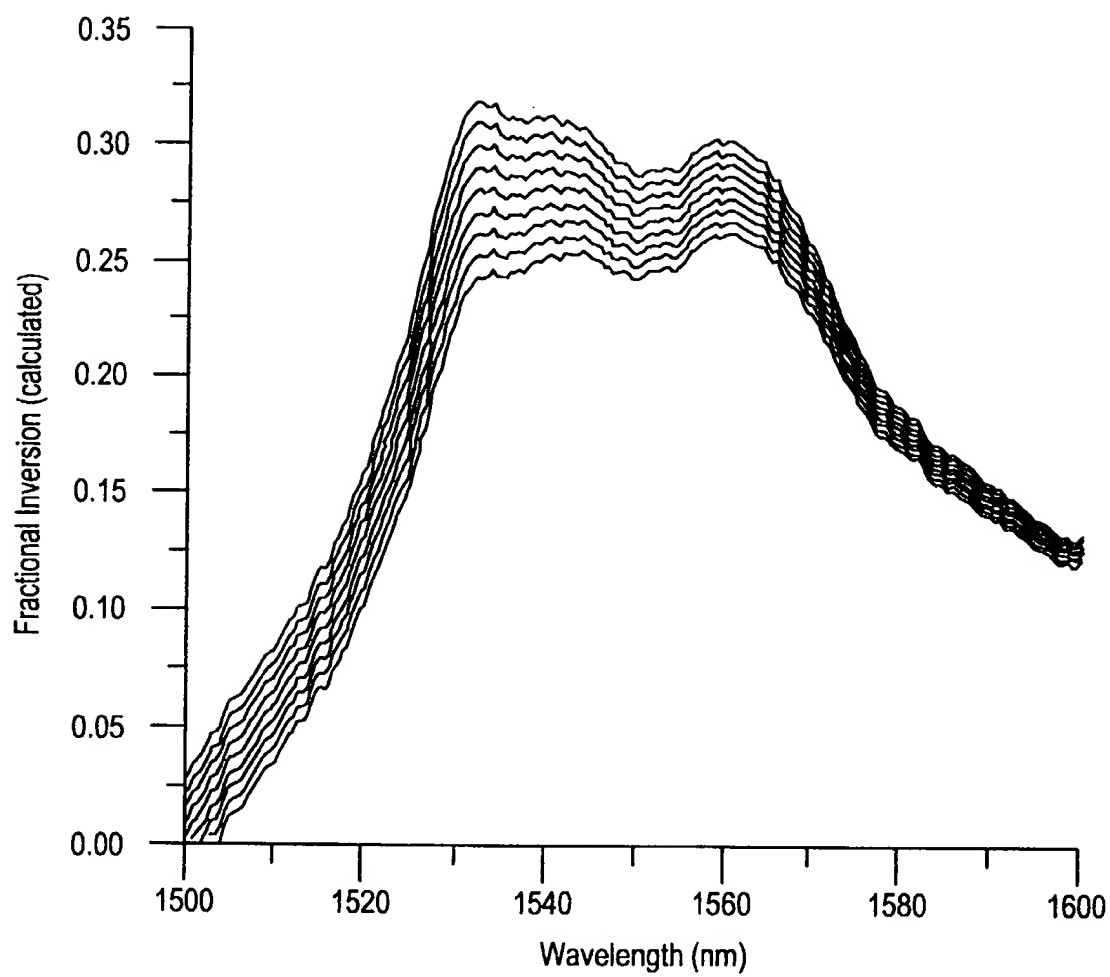


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/07765

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C03C 13/04

US CL :501/37, 41, 64, 73; 385/141, 142

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/37, 41, 64, 73; 385/141, 142

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,274,728 A (TRAN) 28 December 1993 (28-12-93), col. 2, lines 19-43.	1-4, 9-13, 16-28,30,31,36-39
A	US 5,483,628 A (BORRELLI et al) 09 January 1996 (09-01-96).	1-39
A	US 5,537,505 A (BORRELLI et al) 16 July 1996 (16-07-96).	1-39

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

09 JUNE 1999

Date of mailing of the international search report

1

28 JUN 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

KARL GROUP

Telephone No. (703) 308-0661